Chemistry 163B

Colligative Properties

Challenged Penpersonship Notes

colligative

One entry found.

Main Entry: col·li·ga·tive

Pronunciation: kä-lə- gā-tiv, kə- li-gə-tiv

Function: *adjective*

: depending on the number of particles (as molecules) and not on the nature of the particles <pressure is a *colligative property*>

http://www.merriam-webster.com/dictionary/colligative

Handout #55

A. Freezing point depression

B. Boiling Point Elevation

C. Osmotic Pressure

quantitative treatment of colligative properties

I. The pure solvent (component B) is originally in equilibrium in the two phases.

II. Addition of solute (component A) lowers the chemical potential of the solvent in the solution phase

III. Temperature (freezing point depression, boiling point elevation) or pressure (osmotic pressure) must be altered to reestablish equilibrium between the solution and the pure solvent phase.

IV. Obtain relationships between X_A or X_B and change in T or P.

I. pure solvent is originally in equilibrium in the two phases

$$pure\ solid_B^{\bullet} \rightleftarrows pure\ \ell iquid_B^{\bullet} \quad at\ T_f^{\bullet} \quad the\ normal\ melting\ T_{fusion}$$

$$\mu_B^{s\bullet}(T_f^{\bullet}) = \mu_B^{\ell\bullet}(T_f^{\bullet})$$

$$\Delta\mu_B(T_f^{\bullet}) = \mu_B^{\ell\bullet}(T_f^{\bullet}) - \mu_B^{s\bullet}(T_f^{\bullet}) = 0$$

$$\Delta\bar{H}(T_f^{\bullet}) = \Delta\bar{H}_{B\,melting} \quad > 0$$

for solid $\longrightarrow$ liquid

II. Still at $T_f^\bullet$, add solute A to solvent with resulting mole fractions X_A and X_B

for solid phase of B there is no change :

$$\mu_B^{s\bullet}(T_f^\bullet) = \mu_B^{solid}(T_f^\bullet)$$

for the solvent (B) in solution:

$$\mu_B^{\ell}(T_f^\bullet) \equiv \mu_B^{solvent} \equiv \mu_B^{\ell\,(in\,soln)}(T_f^\bullet) = \mu_B^{\ell\bullet}(T_f^\bullet) + RT_f^\bullet \ln\left(\gamma_B X_B\right)$$

so now $\Delta\mu_B(T_f^\bullet) = \mu_B^{\ell}(T_f^\bullet) - \mu_B^{s\bullet}(T_f^\bullet) = \Delta\mu_B^\bullet(T_f^\bullet) + RT_f^\bullet \ln\left(\gamma_B X_B\right)$

where $\Delta\mu_B^\bullet(T_f^\bullet) = \mu_B^{\ell\bullet}(T_f^\bullet) - \mu_B^{s\bullet}(T_f^\bullet)$

and $\Delta\mu_B^\bullet(T_f^\bullet) = 0$ since pure liquid and solid are in equilibrium at $T_f^\bullet$

thus $\Delta\mu_B(T_f^\bullet) = RT_f^\bullet \ln\left(\gamma_B X_B\right) \quad < 0$

> so the forward reacton (melting of the solid) would now occur spontaneously at $T_f^\bullet$

freezing point depression (solid ⇄ solution)

III. Alter temperature to restore equilibrium $T_f^\bullet \rightarrow T_f$

$$\left(\frac{\partial \frac{\Delta\mu}{T}}{\partial T} \right)_P = -\frac{\Delta\bar{H}}{T^2}$$

$$\int_{T_f^\bullet}^{T_f} d\left(\frac{\Delta\mu_B}{T} \right)_P = -\int_{T_f^\bullet}^{T_f} \frac{\Delta\bar{H}_{B\ melting}}{T^2} dT$$

$$\left(\frac{\Delta\mu_B(T_f)}{T_f} \right)_P - \left(\frac{\Delta\mu_B(T_f^\bullet)}{T_f^\bullet} \right)_P = -\int_{T_f^\bullet}^{T_f} \frac{\Delta\bar{H}_{B\ melting}}{T^2} dT$$

old stuff

III. Alter temperature to restore equilibrium *(continued)*

$$\left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P - \left(\frac{\Delta\mu_B(T_f^\bullet)}{T_f^\bullet}\right)_P = -\int_{T_f^\bullet}^{T_f} \frac{\Delta\bar{H}_{B\,melting}}{T^2}\,dT$$

$$\left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P = 0 \text{ since at 'new' equilibrium } T_f \text{ , } \Delta\mu_B(T_f) = 0$$

$$\text{and} \quad \left(\frac{\Delta\mu_B(T_f^\bullet)}{T_f^\bullet}\right)_P = R\ln\left(\gamma_B X_B\right) \quad \text{from eqn in II.}$$

$$-R\ln\left(\gamma_B X_B\right) = -\int_{T_f^\bullet}^{T_f} \frac{\Delta\bar{H}_{B\,melting}}{T^2}\,dT$$

$$R\ln\left(\gamma_B X_B\right) + \left[-\int_{T_f^\bullet}^{T_f} \frac{\Delta\bar{H}_{B\,melting}}{T^2}\,dT\right] = 0$$

change in $\Delta\mu_B$ due to adding solute

change in $\Delta\mu_B$ due to temperature change

IV. Obtain relationships between X_B and change in T

$$R\ln(\gamma_B X_B) = \int_{T_f^\bullet}^{T_f} \frac{\Delta\bar{H}_{B\,melting}}{T^2}\,dT$$

$\Delta\bar{H}_{B\,melting}$ ~ independent of T

$$R\ln(\gamma_B X_B) = -\Delta\bar{H}_{B\,melting}\left[\frac{1}{T_f} - \frac{1}{T_f^\bullet}\right]$$

since *lhs* $< 0 \Rightarrow T_f < T_f^\bullet$ (freezing point **depression**)

$$\boxed{\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{B\,melting}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^\bullet}\right]\right] \quad \text{(integration of eqn 9.31 E\&R)}}$$

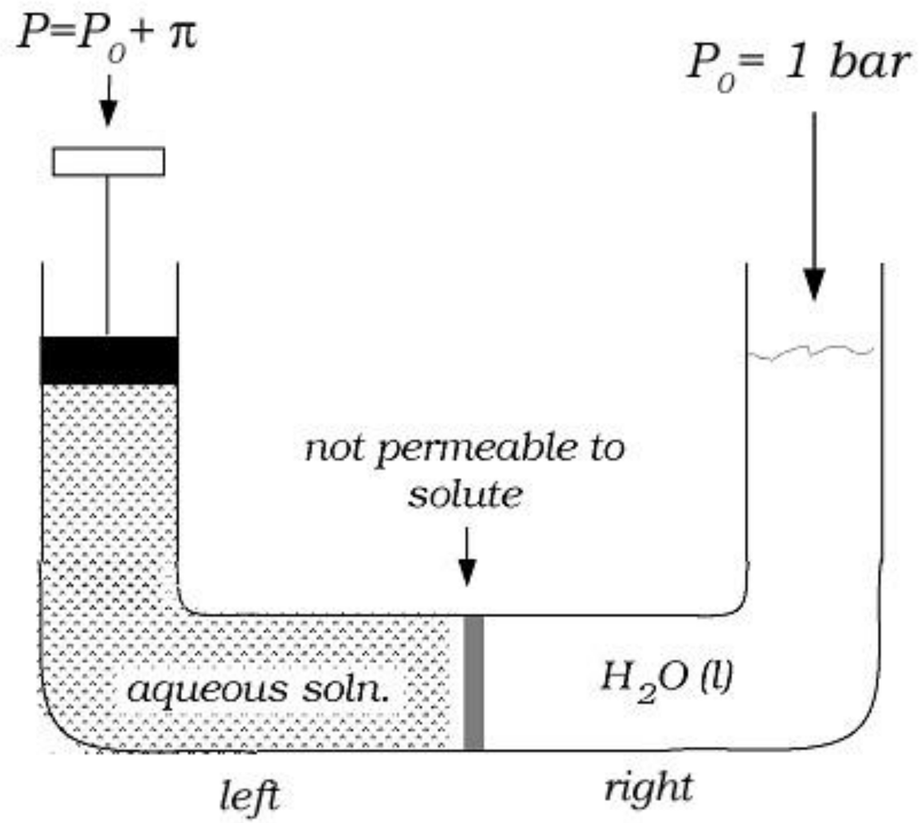
IV. Obtain relationships between X_B and change in T *(cont)*

$$\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{B\,melting}}{R}\left[\frac{1}{T_f}-\frac{1}{T_f^\bullet}\right]\right]$$

$$-\frac{R}{\Delta\bar{H}_{B\,melting}}\ln\left(\gamma_B X_B\right)+\frac{1}{T_f^\bullet}=\frac{1}{T_f}$$

$$T_f = \frac{T_f^\bullet \Delta\bar{H}_{B\,melting}}{\Delta\bar{H}_{B\,melting} - RT_f^\bullet \ln\left(\gamma_B X_B\right)} \qquad \text{(~ eqn 9.32 E\&R)}$$

Osmotic Pressure Equilibrium



I. pure solvent at P_{left} is originally in equilibrium with pure solvent at P_{right} ; i.e. $P_{left}=P_{right}=P_0$

$$pure\ \ell iquid_{B}^{\bullet}(P_0, left) \rightleftarrows pure\ \ell iquid_{B}^{\bullet}(P_0, right) \quad at\ T$$

'left' and 'right' refer to compartments separated by solute impermeable membrane

$$\mu_{\mathrm{B}}^{\bullet}(P_0, left) = \mu_{\mathrm{B}}^{\bullet}(P_0, right)$$

II. in left hand compartment add solute A to solvent
with resulting mole fractions X_A and X_B

$$\textit{add } X_A \textit{ solute to liquid in 'left' compatment resulting in } X_B \textit{ for solvent}$$

$$\mu_B^{\ell}(P_0, left) = \underline{\mu_B^{\ell\bullet}(P_0, left) + RT\ln\left(\gamma_B X_B\right)} < \mu_B^{\ell\bullet}(P_0, right)$$

$$\mu_B^{\ell}(P_0, left) < \mu_B^{\ell\bullet}(P_0, right)$$

so the solvent B moves spontaneously left $\leftarrow$ right

(i.e. diluting solution on left)

III. alter Pressure: $P_{left} \longrightarrow P_0 + \pi$ to restore equilibrium

$$solution\,(X_B, P_0+\pi, left) \rightleftarrows pure\ solvent(P_0, right)$$

$$\left(\frac{\partial \mu_B^{left}}{\partial P}\right)_T = \bar{V}_B$$

$$\int_{P_0}^{P_0+\pi} d\mu_B^{left}(X_B) = \int_{P_0}^{P_0+\pi} \bar{V}_B dP$$

assuming solvent is incompressible

($\bar{V}_B$ doesn't change with pressure at constant T)

$$\mu_B^{left}(X_B, P_0+\pi) = \mu_B^{left}(X_B, P_0) + [P_0+\pi-P_0]\bar{V}_B$$

$$\mu_B^{left}(X_B, P_0+\pi) = \mu_B^{left}(X_B, P_0) + \pi\bar{V}_B$$

osmotic pressure (III, alter pressure, continued)

$$\mu_B^{left}\left(X_B, P_0+\pi\right)=\mu_B^{left}\left(X_B, P_0\right)+\pi\bar{V}_B$$

$$\mu_B^{left}\left(X_B, P_0+\pi\right)=\mu_B^{\bullet}\left(P_0\right)+RT\ln\left(\gamma_B X_B\right)+\pi\bar{V}_B$$

want π to restore equilibrium such that

$$\boldsymbol{\mu_B^{left}}\left(\boldsymbol{X_B}, \boldsymbol{P}_0+\pi\right)=\boldsymbol{\mu_B^{\bullet\, right}}\left(\boldsymbol{P}_0\right)$$

$$\underbrace{\mu_B^{\bullet}\left(P_0\right)+RT\ln\left(\gamma_B X_B\right)+\pi\bar{V}_B}_{left}=\underbrace{\mu_B^{\bullet}\left(P_0\right)}_{right}$$

$$\pi=-\frac{RT\ln\left(\gamma_B X_B\right)}{\bar{V}_B}$$

osmotic pressure (a little more manipulation)

$$\pi = -\frac{RT\ln\left(\gamma_B X_B\right)}{\bar{V}_B}$$

$$for\ \gamma_B \approx 1 \quad and\ X_B = 1 - X_A$$

$$\pi = -\frac{RT\ln\left(1 - X_A\right)}{\bar{V}_B}$$

$$\ln(1+x) \approx x \quad for\ small\ x \quad (i.e.\ dilute\ solution,\ X_A\ small)$$

$$\pi = \frac{X_A RT}{\bar{V}_B}$$

$$X_A = \frac{n_A}{n_A + n_B} \quad and\ n_A + n_B \approx n_B \quad for\ dilute\ solution$$

$$\pi \approx \frac{n_A RT}{n_B \bar{V}_B}$$

$$\pi V_B = n_A RT$$

$$\pi V_{solution} = n_{solute} RT$$

Handout #55 Colligative Properties

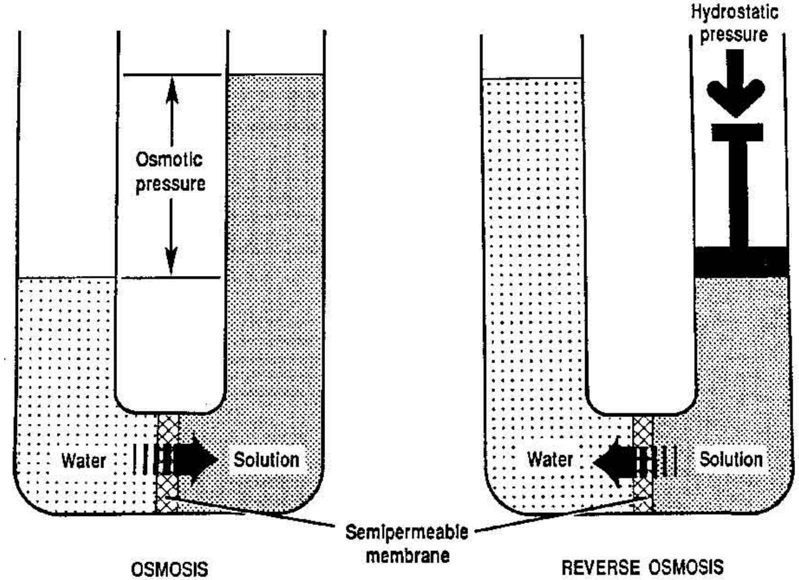
from relationships for Chem 163B final:

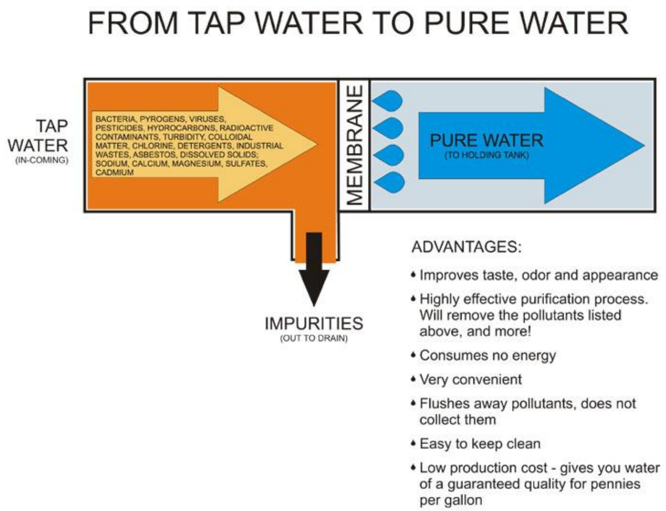
Colligative properties:

:

- freezing point lowering: $\gamma_B X_B = \exp\left[-\frac{\Delta \bar{\bar{H}}_{fusion}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^\bullet}\right]\right]$
- boiling point elevation: $\gamma_B X_B = \exp\left[\frac{\Delta \bar{\bar{H}}_{vaporization}}{R}\left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^\bullet}\right]\right]$
- osmotic pressure: $$\pi = \frac{-RT\ln(\gamma_B X_B)}{\bar{\bar{V}}_B}$$ $$\pi \approx \frac{n_A RT}{V_B} = \frac{n_{solute} RT}{V_{solvent}} \quad \textit{for dilute solution}$$

reverse osmosis





Water Systems
Aqua Technology
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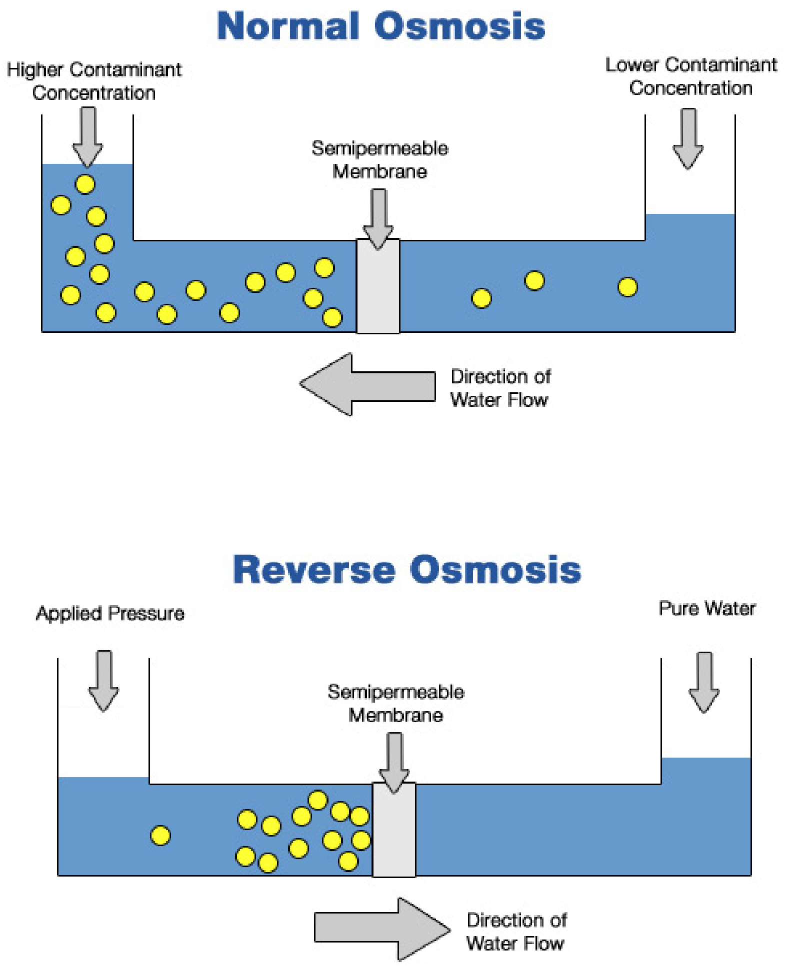
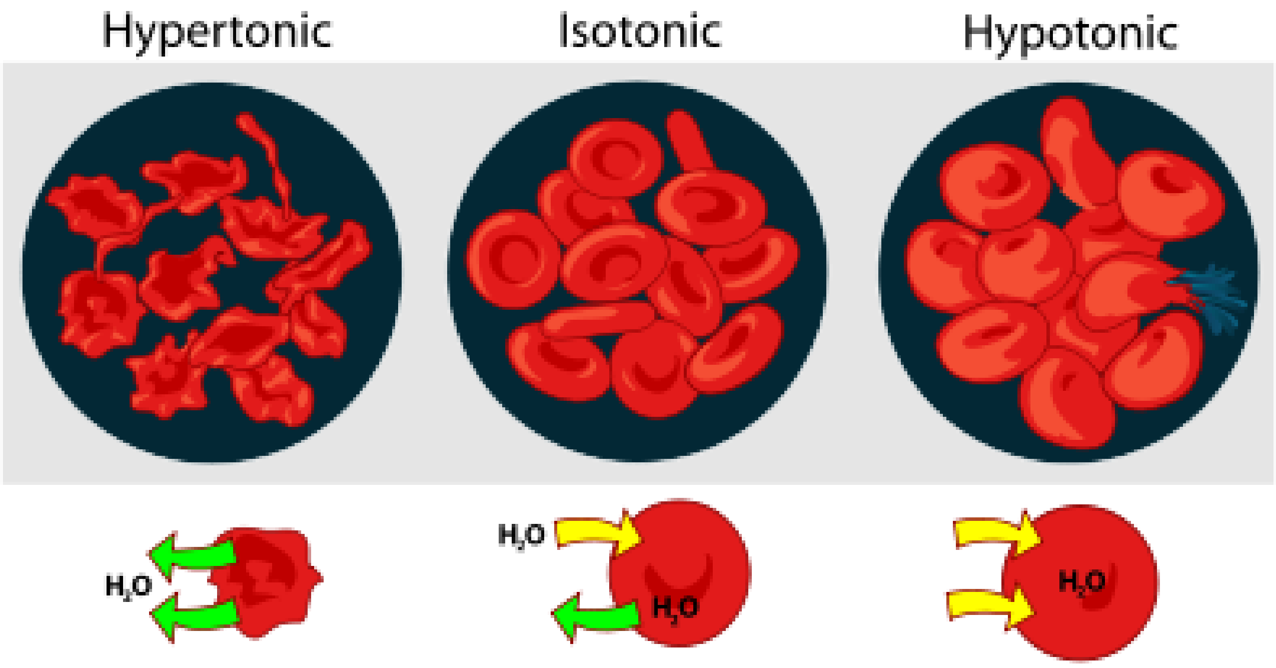
ESP Water Products.com

Reverse Osmosis



http://www.zenon.com/image/resources/glossary/reverse_osmosis/normal_osmosis.jpg

effect of osmosis on blood cells



$$\mu_{H_2O}^{outside} < \mu_{H_2O}^{inside} \qquad \mu_{H_2O}^{outside} = \mu_{H_2O}^{inside} \qquad \mu_{H_2O}^{outside} > \mu_{H_2O}^{inside}$$

$$X_{H_2O}^{outside} < X_{H_2O}^{inside} \qquad\qquad X_{H_2O}^{outside} > X_{H_2O}^{inside}$$

$$X_{salt}^{outside} > X_{salt}^{inside} \qquad X_{salt}^{outside} = X_{salt}^{inside} \qquad X_{salt}^{outside} < X_{salt}^{inside}$$

Woman dies after water-drinking contest

Water intoxication eyed in 'Hold Your Wee for a Wii' contest death

Associated Press
updated 7:24 p.m. PT, Sat., Jan. 13, 2007

SACRAMENTO, Calif. - A woman who competed in a radio station's contest to see how much water she could drink without going to the bathroom died of water intoxication, the coroner's office said Saturday.

Jennifer Strange, 28, was found dead Friday in her suburban Rancho Cordova home hours after taking part in the "Hold Your Wee for a Wii" contest in which KDND 107.9 promised a Nintendo Wii video game system for the winner.

"She said to one of our supervisors that she was on her way home and her head was hurting her real bad," said Laura Rios, one of Strange's co-workers at Radiological Associates of Sacramento. "She was crying and that was the last that anyone had heard from her."

NBC VIDEO

Launch

Woman in water drinking contest dies

Jan. 15: Sacramento Bee reporter Christina Jewett talks to MSNBC-TV's Contessa Brewer about the death of a woman who had competed in a radio station contest.

MSNBC

End of Lecture